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(54) Title: LONG CHAIN BRANCHED POLYMERS AND A PROCESS TO MAKE LONG CHAIN BRANCHED POLYMERS

(57) Abstract

A novel polymer and process for producing polymers incorporating linear long chain side branches are provided. The long chain linear branches occur at a frequency of less than 5.0 branches per 1000 carbon atom of the main polymer chains with at least some branches having a molecular weight greater than the critical molecular weight for entanglement of the polymer. The linear long chain branched polymers are produced by alpha-olefin macromolecule incorporation during bridged metallocene catalyst polymerization in solution and slurry processes. The polymers are characterized by superior processability characteristics of the polymer melts and superior mechanical characteristics of the solid polymers. The polymers are useful for fabrication into a wide variety of articles by conventional fabrication techniques.

TITLE

LONG CHAIN BRANCHED POLYMERS AND A PROCESS TO MAKE LONG
CHAIN BRANCHED POLYMERS

FIELD OF THE INVENTION

This invention relates to the field of long chain
branched polymers and a process to make them.

BACKGROUND OF THE INVENTION

This invention relates to novel polyolefin
polymers, processes for producing such polymers, and
applications for such polymers. The commercial
significance of polyolefin polymers is enhanced by the
variety of forms they may take which often exhibit
different physical properties. These different
properties make polyolefin polymers useful in many
different end use applications. The structural
features of polyolefins that are considered most
significant are molecular weight, which is related to
polymer chain length, the type and tacticity of side-
chain branches, and the distribution of side-chain
branches along the main polymer chains. Over the
years, considerable attention has been given to the
molecular architecture of polyolefins. Polyolefins can
be commercially produced using any one of a number of
processes. The random nature of most polymerization
processes results in a heterogeneous polymer, rather
than a truly homogeneous polymer product. Polyolefins
produced by classical Ziegler-Natta catalysts consist
of mixtures of molecules of different molecular weights
and different amounts of comonomer incorporation.
These differences result from the differences in
catalysts used, and differing rates of comonomer
incorporations. Other factors influencing polymer

products include choice of monomers, catalyst
reactivity or ability to incorporate comonomers, and
differing polymerization process conditions.

Commercial polyethylenes fall into one of two
5   general categories, linear polyethylenes (LPEs) and
"conventional" low density polyethylenes (LDPEs). LPEs
are traditionally produced by addition polymerization
of ethylene, or by the copolymerization of ethylene and
an alpha-olefin comonomer, in a variety of processes
10   using coordination catalysts. LDPEs are traditionally
produced by free-radical polymerization of ethylene in
high temperature and high pressure reactors using
peroxide initiators. These two broad categories of
polyethylenes have significant structural and physical
15   differences. The most important difference between
LPEs and LDPEs is the nature of the side-chain
branching. LDPEs are highly side-chain branched having
dendritic (tree-like) long chain side branches attached
to the main polymer chains. These branches are created
20   as a result of inter-molecular chain transfer during
free-radical polymerization. Dendritic side-chain
branching gives certain advantages, particularly
processing advantages, to the polymer melts. However
these processing advantages are balanced by
25   disadvantages inherent with LDPEs relating to
mechanical properties of the solid polymers such as
lower stiffness, hardness, low tear resistance, low
environmental stress crack resistance (ESCR) and, low
tensile strength. These properties relative to LPEs
30   with equivalent density and melt index properties.

Likewise, LPEs without long chain side branches
have good mechanical properties such as good stiffness,
hardness, tensile strength characteristics, tear
resistance, and ESCR; however, from a processing
35   standpoint, LPEs have the disadvantages of a tendency
to melt fracture and low shear sensitivity resulting in

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high melt viscosity, low melt strength and higher
processing costs.

Polyethylene producers have spent considerable
time and resources over the years trying to produce
5   polymers possessing the polymer melt processing
advantages of LDPEs and the mechanical properties
advantages of solid LPEs. Most efforts have centered
around adding long branches to LPEs. One conventional
method of producing long chain branches in LPEs is to
10 copolymerize ethylene with alpha-omega dienes. This
method is illustrated in U.S. Patent 3,984,610, PCT
application 91-17,194 and Japanese KOKAI 02-261,809,
which are incorporated by reference herein.

In this method, dienes are simultaneously
15 incorporated into propagating chains, thereby creating
a covalent bridge between two linear molecules. The
resulting structure in the vicinity of the bridge is
typically shaped like the letter "H". The resultant
side-chain branches can be long and are usually paired
20 rather than isolated. As the number of dienes per
molecule increases, the complexity of the branching
approaches that of dendritic branching ultimately
causing the polymer to lose its linear mechanical
characteristics. In addition to mechanical properties
25 shortcomings, polymers produced with dienes have
encountered resistance to approval by regulatory
authorities for food contact applications.

Other methods to produce long chain branches on
LPEs involve post-polymerization treatments of linear
30 molecules. Several different types of post-
polymerization treatments have been used. United
Kingdom Patent 901,148 demonstrates the production of
branched polyethylene by treating molten polyethylene
with oxygen. One method of doing this is by forcing
35 air into the molten polyethylene during melt extrusion.
This method of production results in non-linear long
chain branches. United States Patent 4,586,995,

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discloses the irradiation of molten polyethylene in the
absence of oxygen to produce Y branches having two to
fifty carbon chains per ten thousand carbon atoms in
the main polymer chain. United Kingdom Patent

5   1,379,853 discloses the introduction of branches into
polyethylene during the degradation of high density
polyethylene in the presence of an organic peroxide.
This process will result in dendritic side branches.
Finally, Japanese Kokai 59-59,760 discusses the

10   production of long chain branched polyethylene by
heating polyethylene containing a terminal vinyl group
at 180° - 360°C under vacuum conditions or an inert
atmosphere for five minutes to six hours. The polymer
produced has long chain branches with a frequency of

15   3.5 branches per molecule. These branches are non-
linear.
        A third type of process for producing branching in
linear polyethylene is the use of a polymerization
cocatalyst which contains a long chain branched

20   polymeric group. U.S. Patent 4,500,648 and divisionals
thereof disclose high density polyethylene production
with branches prepared by polymerization of ethylene in
the presence of a coordination catalyst containing an
organoaluminum compound having a branched polymeric

25   hydrocarbyl group as one of its substituents. The
polymers produced by this method contain non-linear
long chain branches.
        A method for the preparation of LLDPE using only
ethylene is described in European Application Number

30   87108556.9 EPA 250,999. The method used is the
oligomerization of ethylene using nickel based
catalysts followed by copolymerization of the olefin
mixture with ethylene through use of a chromium
catalyst system. The objective of this application is

35   to utilize a process for preparing higher olefins to
prepare a mixture of olefins which is then
copolymerized to yield the LLDPE structure. The LLDPE

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prepared in this method consists of polyethylene with a
distribution of side-chains having 14 to 200 carbon
atoms. One deficiency of this application is that it
utilizes very low activity catalysts to form the
5   oligomers and the subsequent copolymers. Secondly,
this application does not recognize the importance of
utilizing even longer side-chains than those described
in the application.

        A method for producing LLDPE containing long-chain
10   branches is described in European patent application
91301811.5 EPA 446,013 and Japanese application H1-
251748. EP 91301811.5 presents the polymerization of
ethylene using Nickel complexes to give LLDPE
containing long-chain branching. JP H1-251748 presents
15   the copolymerization of ethylene and hexene using
Nickel based polymerization catalysts. Using the
catalyst systems described in the application, ethylene
copolymers containing short and long chain branches are
produced. The chief limitations of these applications
20   are those known for Nickel based catalyst systems: 1)
the low catalyst activities (30 g polymer/mmol catalyst
in 1 hr); and 2) molecular weight distribution is
proportional to molecular weight, therefore high
molecular weights are accompanied by broad molecular
25   weight distributions. This method does not produce
higher Mw with narrow Mw/Mn.

SUMMARY OF THE INVENTION

        This invention relates to novel polymers and
30   processes for making polymers incorporating linear long
chain side branches. The term "linear" is herein
defined to include side chains that have some side
chain branching but are not dendritic. The linear long
chain branches are comprised of sidechains being at
35   least 250 carbons long, which have molecular weights at
least as great as the critical molecular weight for
entanglement (M_c) of the polymer. The linear long

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chain branches occur at a frequency of less than 5.0
branches per 1000 carbon atoms in the main polymer
chains. The linear long chain branched polymers are
produced by incorporating a macromolecule during
5   metallocene-catalyzed solution polymerization processes
(solvent or bulk process at low, medium or high
pressure). The long chain branched polymers possess
the processability characteristics of conventional long
chain branched polymer melts and the mechanical
10 characteristics of conventional solid linear polymers.
Polymers produced in accordance with this invention are
useful for fabrication into a wide variety of articles
by injection molding, extrusion coating and molding,
blown film, cast film, thermoforming and rotational
15 molding.

DETAILED DESCRIPTION OF THE INVENTION

During traditional coordination-catalyst
polymerization of polyethylenes, most polymer chains
20 are terminated by the beta-abstraction mechanism which
results in terminal unsaturation. If the molecule
terminates after incorporation of a comonomer, the
result is vinylene or vinylidene unsaturation. If the
molecule terminates after the incorporation of
25 ethylene, the result is vinyl unsaturation. A vinyl
unsaturated molecule can be considered a large alpha-
olefin.

Linear copolymers are produced by additional
polymerization of two or more vinyl terminated monomers
30 ranging in size from two to thirty carbon atoms. In
the present invention, copolymers are produced in which
vinyl terminated polymers, also called macromonomers or
macromers, are incorporated into the addition
polymerization reaction along with the monomers. The
35 vinyl terminated polymers responsible for the unique
characteristics of polymers produced in accordance with
the present invention are molecules having molecular

weights greater than the critical molecular weight for
entanglement (M_C) of the polymer into which the vinyl
terminated polymers are incorporated. The M_C for
polyethylene is 3,800. The vinyl terminated polymers

5   of this invention are 250 or more carbon atoms long,
preferably 350 to 3500, even more preferably 300 to
3000, or have a Mw of greater than 6000. Further, the
vinyl terminated polymers of this invention are
incorporated into the growing polymer at an average

10 frequency of no more than 5 long side chains per 1000
carbon atoms along the main chain, preferably the
average frequency is 0.2 to 3 long side chains per 1000
carbon atoms, more preferably 0.9 to 2 long side chains
per carbon atoms.

15   Using traditional coordination catalyst processes,
these vinyl terminated polymers do not incorporate into
growing polymer chains. The inventors have discovered
that using certain metallocene catalysts, preferably
under solution process conditions, in accordance with

20 the present invention will result in these vinyl
terminated polymers being incorporated into growing
polymer chains at controllable amounts of
incorporation.   As these vinyl terminated polymers are
incorporated into propagating polymer chains, they

25 become isolated long chain branches of that polymer
chain. The inventors have found that long chain
branches, in accordance with the present invention,
yield polymers having the positive mechanical
attributes of solid linear polyolefins, while having

30 the positive processing characteristics of melts of
branched polyolefins.

        The vinyl terminated polymers of this invention
which eventually become side chains can be homopolymers
or copolymers of one or more C_2 to C_{30} olefin,

35 preferably alpha olefins, even more preferably homo or
copolymers of ethylene, propylene, 1-butene, 1-pentene,
1-hexene, 1-octene and 4-methylpentene-1. Cyclic

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olefins are also useful monomers in the practice of
this invention. Likewise, the main chain can also be a
homopolymer or copolymer of one or more C_2 to C_{30}
olefins, preferably alpha olefins, even more preferably
5   homo or copolymers of ethylene, propylene, butene-1,
pentene-1, hexene-1, octene-1 and 4-methyl-pentene-1.
Copolymer is herein defined to include polymers of 2 to
4 different monomers and block copolymers of any of the
above olefins or alpha olefins.
10   The vinyl terminated polymers useful in this
invention can be prepared using a variety of
metallocene catalysts and process conditions. The
particular choice of catalyst and process conditions
depends upon the desired polymer composition and
15   molecular weights. High vinyl termination content is
necessarily preferred. Preferably about 0.9 to about
1.1 chain end unsaturations per macromer are present,
even more preferably about 1 chain end unsaturation per
macromer. Conditions which favor their formation are
20   high temperatures, no comonomer, no transfer agents
like hydrogen, and a non-solution process or a
dispersion using an alkane diluent. Thus the
metallocene should be active at relatively high
temperatures. The selected metallocene may also be
25   thermally activated to yield the beta-hydrogen
eliminated product; vinyl ends. Thus one could prepare
materials at low temperature then increase the
temperature to get the beta-hydride eliminated product.
The steric requirements of the metallocene will affect
30   the degree to which copolymerization occurs.
Metallocenes which possess steric hindrance will yield
vinyl terminated polymers which are relatively free of
branches when compared to metallocenes which do not
possess this hindrance.
35   Another method producing vinyl termination
involves production of polymer with an ethylene "cap"
or end with the needed vinyl group. This could be

accomplished by beginning polymerization at a low
temperature, for example, below zero degrees Celsius,
and raising the reaction temperature at the "end" of
the reaction, for example, to above ten degrees

5   Celsius, and simultaneously adding ethylene so that the
ethylene preferentially polymerizes to form an end
"cap" or block. A block copolymer of ethylene and a C_3
to C_{30} alpha olefin would also present the necessary
vinyl termination.

10   The vinyl terminated polymers can be optimally
copolymerized using metallocenes which are sterically
unhindered. In addition the polymerization system
should be a single-phase, or if two-phase, the vinyl
terminated polymers must be sufficiently mobile to

15   permit their copolymerization. The preferred process
for their copolymerization is a solution process. Thus
the process solvent and temperature preferred are those
in which the vinyl terminated polymer is soluble or
substantially swollen.

20   The present invention preferably utilizes catalyst
system comprising a metallocene catalyst with
cocatalyst activators of an alumoxane or a "non-
coordinating" anion. The metallocene catalyst is an
activated cyclopentadienyl group 4 transition metal

25   compound. In particular, the metallocene catalysts
employed in this invention are organometallic
coordination compounds which are cyclopentadienyl
derivatives of group 4 metals of the periodic table of
the elements and include mono-, di- and tri-

30   cyclopentadienyls and their derivatives. Particularly
desirable are the metallocenes of the group 4 metals:
titanium, zirconium and hafnium. The cyclopentadienyl
metallocenes of this invention can be activated with
either an alumoxane or a "non-coordinating" anion-type

35.   activator. In general at least one metallocene
compound is employed in formation of the catalyst
system. Metallocenes employed in accordance with this

10

invention contain at least one cyclopentadienyl ring
and preferably comprise titanium, zirconium, or
hafnium, most preferably hafnium, or zirconium for bis-
cyclopentadienyl compounds and titanium for mono-
5   cyclopentadienyl compounds. The cyclopentadienyl ring
can be substituted or unsubstituted or contain one or
more substituents e.g. from 1 to 5 substituents such as
for example, hydrocarbyl substituent e.g. up to five C_1
to C_{20} hydrocarbyl substituents or other substituents
10   e.g. for example, a trialkyl cyclic substituent. A
metallocene may contain 1, 2 or 3 cyclopentadienyl
rings, however, two rings are preferred for use with
hafnium or zirconium. One ring is preferred for use
with titanium.
15   The catalyst system used in this invention can be
described as comprising cyclopentadienyl transition
metal catalyst having at least one delocalized pi-
bonded moiety and an activating cocatalyst. The
catalyst system used in this invention can also be
20   described as comprising a cyclopentadienyl transition
metal catalyst of a transition metal compound
containing a single cyclopentadienyl group and a
heteroatom containing group each bonded to the
transition metal, said cyclopentadienyl group and
25   heteroatom containing groups optionally bridged through
a divalent moiety and an activating cocatalyst.
         In another embodiment of the present invention the
macromonomer can be polymerized in a gas phase process.
This may be achieved by pre-polymerizing the
30   macromonomer by one of many methods known in the art.
For example, the method for supporting a catalyst known
in U.S. Patent Application 885,170 filed 5-18-92,
incorporated by reference, discloses how to place a
catalyst on a support. This supported catalyst can
35   then be combined with the macromonomer under
appropriate polymerization conditions to pre-polymerize
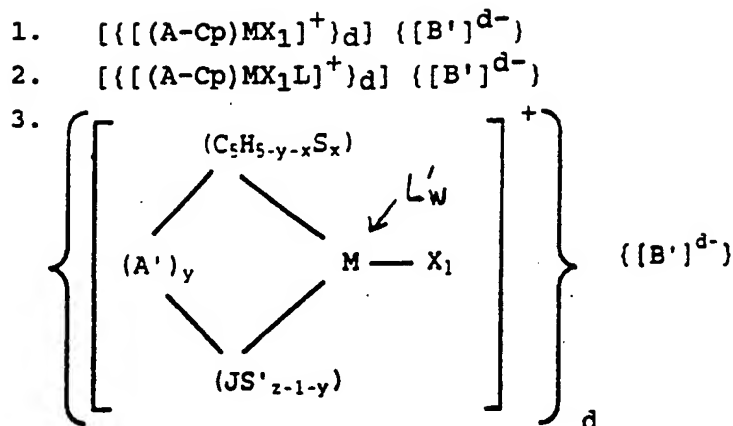the macromonomer with the supported catalyst. This

combination can then be introduced into a gas phase
polymerization reactor to produce long chain branched
polymers in this invention.

5   This macromonomer may also be pre-polymerized with
        other traditional gas phase supported catalysts and
        similarly introduced into the gas phase polymerization
        reactor. Likewise, one could use a two step process
        wherein the macromonomer or the catalyst is first
        placed on support using techniques known in the art and
10   then the catalyst and/or the macromoner are added later
        to form the supported pre-polymerized catalyst
        combination. As is well know in the art, the pre-
        polymerization process is normally a slow, controlled
        process to initiate controlled polymer fracture or
15   support fracture thus, one of ordinary skill in the art
        would be sure to maintain appropriate reaction
        conditions such as temperatures from 40°C to 140°C in a
        suitable solvent with the introduction of ethylene, or
        suitable comonomers to form the macromonomers in a
20   controlled amount.

Ionic Catalyst System - General Description

        The process of this invention is practiced with
        that class of ionic catalysts referred to, disclosed,
25   and described in European Patent Applications EP 0 277
        003 A1 and EP 0 277 004 A1, and PCT Application WO
        92/00333, and U.S. Patents 5,055,438 and 5,096,867,
        which are herein incorporated by reference. The ionic
        catalysts used in this invention can be represented by
30   one of the following general formulae (all references
        to groups being the new group notation of the Periodic
        Table of the Elements as described by Chemical and
        Engineering News, 63(5), 27, 1985):

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1. $[\{[(A\text{-}Cp)MX_1]^+\}_d]$ $\{[B']^{d-}\}$

2. $[\{[(A\text{-}Cp)MX_1L]^+\}_d]$ $\{[B']^{d-}\}$

3.

$$\left\{\left[\begin{array}{c} (C_5H_{5-y-x}S_x) \\ \diagup \quad \diagdown \quad \swarrow L'_W \\ (A')_y \qquad\qquad M \!-\! X_1 \\ \diagdown \quad \diagup \\ (JS'_{z-1-y}) \end{array}\right]^+\right\}_d \{[B']^{d-}\}$$

wherein:

(A-Cp) is either (Cp) (Cp*) or Cp-A'-Cp*; Cp and Cp* are the same or different cyclopentadienyl rings substituted with from zero to five substituent groups S, each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted Group 15 element, substituted Group 16 element or halogen radicals, or Cp and Cp* are cyclopentadienyl rings in which any two adjacent S groups are joined forming a C4 to C20 ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

A' is a bridging group, which group may serve to restrict rotation of the Cp and Cp* rings or $(C_5H_{5-y-x}S_xx)$ and $JS'_{(z-1-y)}$ groups;

$(C_5H_{5-y-x}S_x)$ is a cyclopentadienyl ring substituted with from zero to five S radicals;

x is from 1 to 5 denoting the degree of substitution;
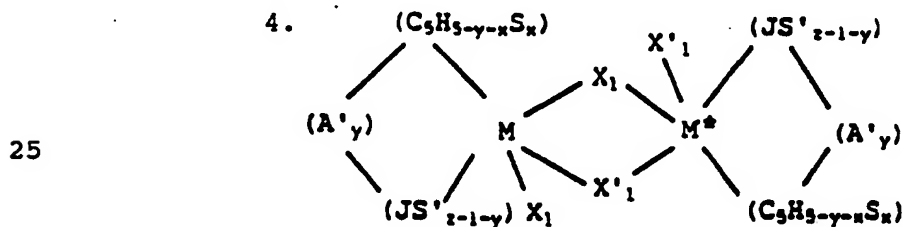
M is titanium, zirconium, or hafnium;

X_1 is a hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, hydrocarbyl-substituted organometalloid radical or halocarbyl-

substituted organometalloid radical which radical may optionally be covalently bonded to both or either M and L or all or any M, S, or S';

    (JS_{z-1-y}) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2; S is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

    y is 0 or 1;

    L is an olefin, diolefin or aryne ligand, or a neutral Lewis base; L' can also be a second transition metal compound of the same type such that the two metal center M and M* are bridged by X_1 and X'_1, wherein M* has the same meaning as M and X'_1 has the same meaning as X_1 where such dimeric compounds which are precursors to the cationic portion of the catalyst are represented by the formula:

4.

$$
\begin{array}{c}
(C_5H_{5-y-x}S_x) \qquad\qquad X'_1 \qquad\qquad (JS'_{z-1-y}) \\[4pt]
\diagup\;\;\;\diagdown\qquad\diagup\;\;\diagdown\qquad\diagup\;\;\;\diagdown \\[2pt]
(A'_y)\qquad\; M \qquad\qquad M^* \qquad\;\; (A'_y) \\[2pt]
\diagdown\;\;\diagup\;\diagdown\qquad\diagup\;\;\;\diagdown\qquad\diagup \\[2pt]
(JS'_{z-1-y})\; X_1 \qquad X'_1 \qquad (C_5H_{5-y-x}S_x)
\end{array}
$$

    w is an integer from 0 to 3;

    B is a chemically stable, non-nucleophilic anionic complex having a molecular diameter about or greater than 4 angstroms or an anionic Lewis-acid activator resulting from the reaction of a Lewis-acid activator with the precursor to the cationic portion of the catalyst system described in formulae 1-4. When B' is a Lewis-acid activator, X_1 can also be an alkyl group donated by the Lewis-acid activator; and

    d is an integer representing the charge of B.

The improved catalysts are preferably prepared by combining at least two components. In one preferred method, the first component is a cyclopentadienyl derivative of a Group 4 metal compound containing at

5   least one ligand which will combine with the second component or at least a portion thereof such as a cation portion thereof. The second component is an ion-exchange compound comprising a cation which will irreversibly react with at least one ligand contained

10   in said Group 4 metal compound (first component) and a non-coordinating anion which is either a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or

15   metalloid atom or an anion comprising a plurality of boron atoms such as polyhedral boranes, carboranes and metallacarboranes.

In general, suitable anions for the second component may be any stable and bulky anionic complex

20   having the following molecular attributes: 1) the anion should have a molecular diameter greater than 4 Å; 2) the anion should form stable ammonium salts; 3) the negative charge on the anion should be delocalized over the framework of the anion or be localized within

25   the core of the anion; 4) the anion should be a relatively poor nucleophile; and 5) the anion should not be a powerful reducing to oxidizing agent. Anions meeting these criteria - such as polynuclear boranes, carboranes, metallacarboranes, polyoxoanions and

30   anionic coordination complexes are well described in the chemical literature.

The cation portion of the second component may comprise Bronsted acids such as protons or protonated Lewis bases or may comprise reducible Lewis acids such

35   as ferricinum, tropylium, triphenylcarbenium or silver cations.

In another preferred method, the second component
is a Lewis-acid complex which will react with at least
one ligand of the first component, thereby forming an
ionic species described in formulae 1-4 with the ligand

5   abstracted from the first component now bound to the
second component. Alumoxanes and especially
methylalumoxane, the product formed from the reaction
of trimethylaluminum in an aliphatic or aromatic
hydrocarbon with stoichiometric quantities of water,

10   are particularly preferred Lewis-acid second
components.

Upon combination of the first and second
components, the second component reacts with one of the
ligands of the first component, thereby generating an

15   ion pair consisting of a Group 4 metal cation and the
aforementioned anion, which anion is compatible with
and "non-coordinating" toward the Group 4 metal cation
formed from the first component. The anion of the
second compound must be capable of stabilizing the

20   Group 4 metal cation's ability to function as a
catalyst and must be sufficiently labile to permit
displacement by an olefin, diolefin or an
acetylenically unsaturated monomer during
polymerization. The catalysts of this invention may be

25   supported. U.S. Patents 4,808,561, issued 2-28-89;
4,897,455 issued 1-3-90; 5,057,475 issued 10-15-91; and
U.S. Patent Application 459,921 (published as PCT
International publication WO 91/09882) disclose such
supported catalysts and the methods to produce such and

30   are herein incorporated by reference.

A.   The Metallocene Component

The Group 4 metal compounds; i.e., titanium,
zirconium, and hafnium metallocene compounds, useful as

35   first compounds in the preparation of the improved
catalyst of this invention are cyclopentadienyl
derivatives of titanium, zirconium and hafnium. In

general, useful titanocenes, zirconocenes, and
hafnocenes may be represented by the following general
formulae:

5. $(A-Cp)MX_1X_2$

5
6. $(A-Cp)ML$

7. $(Cp*)(CpR)MX_1$

8.

$$
\begin{array}{c}
(C_5H_{5-y-x}S_x) \\
\diagup \quad \diagdown \qquad \diagup (L')_w \\
(A')_y \qquad\qquad M \!\!-\!\! X_1 \\
\diagdown \quad \diagup \qquad \diagdown X_2 \\
(JS'_{z-1-y})
\end{array}
$$

10

wherein:

15   (A-Cp) is either (Cp)(Cp*) or Cp-A'-Cp*; Cp and
Cp* are the same or different cyclopentadienyl rings
substituted with from zero to five substituent groups
S, each substituent group S being, independently, a
radical group which is a hydrocarbyl, substituted-
20   hydrocarbyl, halocarbyl, substituted-halocarbyl,
hydrocarbyl-substituted organometalloid, halocarbyl-
substituted organometalloid, disubstituted boron,
disubstituted Group 15 elements, substituted Group 16
elements or halogen radicals, or Cp and Cp* are
25   cyclopentadienyl rings in which any two adjacent S
groups are joined forming a C_4 to C_{20} ring to give a
saturated or unsaturated polycyclic cyclopentadienyl
ligand;

        R is a substituent on one of the cyclopentadienyl
30   radicals which is also bonded to the metal atom;

        A' is a bridging group, which group may serve to
restrict rotation of the Cp and Cp* rings or
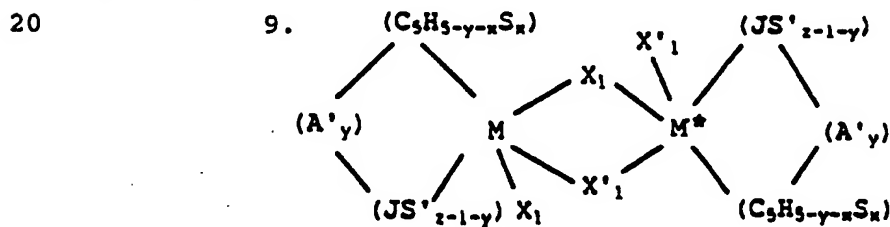$(C_5H_{5-y-x}S_x)$ and $JS'_{(z-1-y)}$ groups;

        y is 0 or 1;

35        $(C_5H_{5-y-x}S_x)$ is a cyclopentadienyl ring
substituted with from zero to five S radicals;

17

x is from 1 to 5 denoting the degree of substitution;

(JS_{z-1-y}) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2, S is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

L is an olefin, diolefin or aryne ligand, or a neutral Lewis base; L' can also be a second transition metal compound of the same type such that the two metal centers M and M* are bridged by X_1 and X'_1, wherein M* has the same meaning as M and X'_1 has the same meaning as X_1 where such dimeric compounds which are precursors to the cationic portion of the catalyst are represented by formula 4;

9.

$$
\begin{array}{ccccc}
 & (C_5H_{5-y-x}S_x) & & X'_1 & (JS'_{z-1-y}) \\
 & \diagup \quad \diagdown & \diagdown X_1 \diagdown & \diagup \diagup & \\
(A'_y) & \quad M & & M^* & (A'_y) \\
 & \diagdown \quad \diagup & \diagup X'_1 & \diagdown & \diagup \\
 & (JS'_{z-1-y}) \; X_1 & & (C_5H_{5-y-x}S_x) &
\end{array}
$$

wherein:

w is an integer from 0 to 3; and

X_1 and X_2 are, independently, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals, disubstituted Group 15 element radicals, or substituted Group 16 element radicals; or X1 and X2 are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or X_1 and X_2 together can be an olefin, diolefin or aryne ligand; or when

Lewis-acid activators are used, X_1 and X_2 can also be joined to form a anionic chelating ligand or can independently be any mono-valent anionic ligand including halides.

5   Table 1 depicts representative constituent moieties for the metallocene components of formulae 6-9. The list is for illustrative purposes only and should not be construed to be limiting in any way. A number of final components may be formed by permuting

10   all possible combinations of the constituent moieties with each other. Illustrative compounds of the formula 6 type are: bis(cyclopentadienyl)hafnium dimethyl, ethylenebis(tetrahydroindenyl)zirconium dihidryde, bis(pentamethyl)zirconium ethylidene, dimethylsilyl(1-

15   fluorenyl)(cyclopentadienyl)titanium dichloride and the like. Illustrative compounds of the formula 7 type are: bis(cyclopentadienyl) (1,3-butadiene(zirconium), bis(cyclopentadienyl) (2,3-dimethyl-1,3-butadiene) zirconium, bis(pentamethylcyclopentadienyl) (benzene)

20   zirconium, bis(pentamethylcyclopentadienyl) titanium ethylene and the like. Illustrative compounds of the formula 8 type are: (pentamethylcyclopentadienyl) (tetramethylcyclopentadienylmethylene) zirconium hydride, (pentamethylcyclopentadienyl)

25   (tetramethylcyclopentadienyl)-(tetramethylcyclopentadienylmethylene) zirconium phenyl and the like. Illustrative compounds of the formula 9 type are: dimethylsilyl(tetramethylcyclopentadienyl) (t-butylamido)zirconium dichloride,

30   ethylene(methylcyclopentadienyl) (phenylamido)titanium dimethyl, methylphenylsilyl(indenyl)(phenyphosphido)hafnium dihydride and (pentamethylcyclopentadienyl) (di-t-butylamido)hafnium dimethoxide.

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For illustrative purposes, the above compounds and those permuted from Table 1 include the neutral Lewis base ligand (L'). The conditions under which complexes containing neutral Lewis base ligands such as ether or
5 those which form dimeric compounds is determined by the steric bulk of the ligands about the metal center. For example, the t-butyl group in $Me_2Si(Me_4C_5)(N-t-Bu)ZrCl_2$ has greater steric requirements that the phenyl group in $Me_2Si(Me_4C_5)(NPh)ZrCl_2Et_2O$ thereby not permitting
10 ether coordination in the former compound in its solid state. Similarly, due to the decreased steric bulk of the trimethylsilylcyclopentadienyl group in $[Me_2Si(Me_3SiC_5H_3)(N-t-Bu)ZrCl_2]_2$ versus that of the tetramethylcyclopentadienyl group in
15 $Me_2Si(Me_4C_5)(N-t-Bu)ZrCl_2$, the former compound is dimeric and the latter is not.

TABLE 1

(A')	(C₅H(5-y-x)Sx)	(JS'z-1-y)	(B - Lewis Acid) X₁ or X₂	M	L or L'
dimethylsilyl	cyclopentadienyl	t-butylamido	hydride	zirconium	ethylene
diethylsilyl	3,4-dimethylcyclopentadienyl	phenylamido	methyl	hafnium	propylene
di-n-propylsilyl	2,5-dimethylcyclopentadienyl	p-n-butylphenylamido	ethyl	titanium	1-butene
di-isopropylsilyl	2-indenyl	cyclohexylamido	phenyl		1,4-hexadiene
di-n-butylsilyl	3,4-diethylcyclopentadienyl	perflurophenylamido	n-propyl		1,3-butadiene
di-t-butylsilyl	2,5-diethylcyclopentadienyl	n-butylamido	isopropyl		1,3-hexadiene
di-n-hexylsilyl	tetramethylcyclopentadienyl	methylamido	n-butyl		acetylene
methylphenylsilyl	tetraethylcyclopentadienyl	ethylamido	amyl		methylacetylene
ethylmethylsilyl	tetraphenylcyclopentadienyl	n-propylamido	isoamyl		benzyne
diphenylsilyl	tetra-n-propylcyclopentadienyl	isopropylamido	hexyl		diethylether
di(p-t-butylphenethylsilyl)	3,4-di-n-butylcyclopentadienyl	benzylamido	isobutyl		dimethylether
n-hexylmethylsilyl	3,4-dicyclohexylcyclopentadienyl	cyclododecylamido	heptyl		trimethylamine
cyclopentamethylenesilyl	2,5-di-n-butylcyclopentadienyl	s-butylamido	octyl		triphenylamine
cyclotetramethylenesilyl	2,5-dicyclohexylcyclopentadienyl	t-butylphosphido	nonyl		triethylamine
cyclotrimethylenesilyl	3-n-octyl-4-n-hexylcyclopentadienyl	ethylphosphido	decyl		triphenyl-phosphine
dimethylgermanyl	2-tetrahydroindenyl	phenylphosphido	cetyl		tetrahydrofuran
diethylgermanyl	3-ethyl-4-n-propylcyclopentadienyl	cyclohexylphosphido	chloro		thiophene
phenylamido	3-isopropyl-4-t-butylcyclopentadienyl	oxo	fluoro		dimethylsulfide
t-butylamido	3-phenyl-4-benzylcyclopentadienyl	sulfido	bromo		
methylamido	3,4-diphenylcyclopentadienyl	methoxide	iodo		
t-butylphosphido	2,5-diphenylcyclopentadienyl	ethoxide	methoxy		
ethylphosphido	3,4-bis(trimethylgermyl)cyclopentadienyl	methylthio	ethoxy		
phenylphosphido	3,4-bis(triethylstanny)cyclopentadienyl	ethylthio	propoxy		
methylene	2-ethyl-5-n-propylcyclopentadienyl	dimethylamide	butoxy		
dimethylmethylene	2-methyl-5-t-butylcyclopentadienyl	diphenylamide	phenoxy		
diethylmethylene	2,5-bis(trifluoromethyl)cyclopentadienyl	methylphenylamide	dimethylamido		
ethylene	3,4-bis(trimethylsilyl)cyclopentadienyl	dicyclohexylphosphido	diethylamido		
dimethylethylene	3,4-bis(N,N-dimethylamido)-cyclopentadienyl	diphenylphosphido	methylethylamido		
dipropylethylene	3,4-bis(dimethylphosphido)-cyclopentadienyl	bis(trimethylsilyl)-amido	diphenylamido		
propylene	3,4-dimethoxycyclopentadienyl	trimethylsilyloxide	diphenylphosphido		
dimethylpropylene	2,5-dimethoxycyclopentadienyl		dicyclohexylphosphido		
diethylpropylene	2,5-dimethyl-3,4-diethylcyclopentadienyl		dimethylphosphido		
1,1-dimethyl-3,3-dimethyl propylene	2,5-diethyl-3,4-dimethylcyclopentadienyl		ethyleneglycol dianion (both X)		
tetramethyldisiloxane	2,5-dimethyl-3,4-di-t-butyl-cyclopentadienyl		methylidene (both X)		
1,1,4,4-tetramethyldisilyl ethylene			ethylidene (both X)		
			propylidene (both X)		

B.   The Activator Component

Ionic catalysts can be prepared by reacting a transition metal compound with some neutral Lewis acids, such as $B(C_6F_6)_3$ or an alumoxane, which upon reaction with the hydrolyzable ligand (X) of the transition metal compound forms an anion, such as $([B(C_6F_5)_3(X)]^-)$, which stabilizes the cationic transition metal species generated by the reaction.   Ionic catalysts can be, and preferably are, prepared with activator components which are ionic compounds or compositions.

Compounds useful as an activator component in the preparation of the ionic catalyst systems used in the process of this invention comprise a cation, which is preferably a Bronsted acid capable of donating a proton, and a compatible non-coordinating anion which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 4 cation) which is formed when the two compounds are combined and said anion will be sufficiently labile to be displaced by olefinic diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers, nitriles and the like.   Two classes of compatible non-coordinating anions have been disclosed in copending U.S. Patent Application Nos. 133,052 and 133,480:   1) anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core, and 2) anions comprising a plurality of boron atoms such as carboranes, metallacarboranes and boranes.

In general, the activator compounds containing single anionic coordination complexes which are useful in this invention may be represented by the following general formula:

10. $[(L''-H)^+]_d[(M')^{m+}Q_1...Q_n]^{d-}$

wherein:

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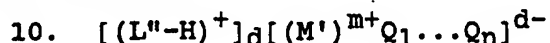
H is a hydrogen atom;

[L"-H] is a Bronsted acid;

M' is a metal or metalloid;

Q_1 to Q_n are, independently, bridged or unbridged
hydride radicals, dialkylamido radicals, alkoxide and
aryloxide radicals, hydrocarbyl and substituted-
hydrocarbyl radicals, halocarbyl and substituted-
halocarbyl radicals and hydrocarbyl and halocarbyl-
substituted organometalloid radicals and any one, but
not more than one, of Q_1 to Q_n may be a halide radical;

m is an integer representing the formal valence
charge of M; and

n is the total number of ligands q.

As indicated above, any metal or metalloid capable of
forming an anionic complex which is stable in water may
be used or contained in the anion of the second
compound. Suitable metals, then, include, but are not
limited to, aluminum, gold, platinum and the like.
Suitable metalloids include, but are not limited to,
boron, phosphorus, silicon and the like. Compounds
containing anions which comprise coordination complexes
containing a single metal or metalloid atom are, of
course, well known and many, particularly such
compounds containing a single boron atom in the anion
portion, are available commercially. In light of this,
salts containing anions comprising a coordination
complex containing a single boron atom are preferred.

The preferred activator compounds comprising boron
may be represented by the following general formula:

11. $[L"-H]^+[BAr_1Ar_2X_3X_4]^-$

wherein:

B is a boron in a valence state of 3;

Ar_1 and Ar_2 are the same or different aromatic or
substituted-aromatic hydrocarbon radicals containing
from about 6 to about 20 carbon atoms and may be linked
to each other through a stable bridging group; and

23

X_3 and X_4 are, independently, hydride radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals, hydrocarbyl- and halocarbyl-substituted organometalloid

5   radicals, disubstituted Group 15 element radicals, substituted Group 16 element radicals and halide radicals, with the proviso that X_3 and X_4 will not be halide at the same time.

In general, Ar_1 and Ar_2 may, independently, be any

10   aromatic or substituted-aromatic hydrocarbon radical. Suitable aromatic radicals include, but are not limited to, phenyl, naphthyl and anthracenyl radicals. Suitable substituents on the substituted-aromatic hydrocarbon radicals, include, but are not necessarily

15   limited to, hydrocarbyl radicals, organometalloïd radicals, alkoxy and aryloxy radicals, alkylamido radicals, fluorocarbyl and fluorohydrocarbyl radicals and the like such as those useful as X_3 and X_4. The substituent may be ortho, meta or para, relative to the

20   carbon atoms bonded to the boron atom. When either or both X_3 and X_4 are a hydrocarbyl radical, each may be the same or a different aromatic or substituted-aromatic radical as are Ar_1 and Ar_2, or the same may be a straight or branched alkyl, alkenyl or alkynyl

25   radical, a cyclic hydrocarbon radical or an alkyl-substituted cyclic hydrocarbon radical. X_3 and X_4 may also, independently be alkoxy or dialkylamido radicals wherein the alkyl portion of said alkoxy and dialkylamido radicals, hydrocarbyl radicals and

30   organometalloid radicals and the like. As indicated above, Ar_1 and Ar_2 could be linked to either X_3 or X_4. Finally, X_3 and X_4 may also be linked to each other through a suitable bridging group.

Illustrative, but non-limiting, examples of boron

35   compounds which may be used as an activator component in the preparation of the improved catalysts of this invention are trialkyl-substituted ammonium salts such

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as triethylammonium tetra(phenyl)boron,
tripropylammonium tetra(phenyl)boron, tri(n-
butyl)ammonium tetra(phenyl)boron, trimethylammonium
tetra(p-tolyl)boron, trimethylammonium tetra(o-

5   tolyl)boron, tributylammonium
tetra(pentafluorophenyl)boron, tripropylammonium
tetra(o,p-dimethylphenyl)boron, tributylammonium te-
tra(m,m-dimethylphenyl)boron, tributylammoniumtetra(p-
tri-fluoromethylphenyl)boron, tri(n-butyl)ammonium

10   tetra(o-tolyl)boron and the like; N,N-dialkyl anilinium
salts such as N,N-dimethylanilinium
tetra(pentafluorophenyl)boron, N,N-diethylanilinium
tetra(phenyl)boron, N,N-2,4,5-pentamethylanilinium
tetra(phenyl)boron and the like; dialkyl ammonium salts

15   such as di(i-propyl)ammonium
tetra(pentafluorophenyl)boron, dicyclohexylammonium
tetra(phenyl)boron and the like; and triaryl
phosphonium salts such as triphenylphosphonium
tetra(phenyl)boron, tri(methylphenyl)phosphonium

20   tetra(phenyl)boron, tri(dimethylphenyl)phosphonium
tetra(phenyl)boron and the like.

Similar lists of suitable compounds containing
other metals and metalloids which are useful as
activator components may be made, but such lists are

25   not deemed necessary to a complete disclosure. In this
regard, it should be noted that the foregoing list is
not intended to be exhaustive and that other useful
boron compounds as well as useful compounds containing
other metals or metalloids would be readily apparent to

30   those skilled in the art from the foregoing general
equations.

The most preferred activator compounds comprising
boron may be represented by the following general
formula:

35   12. $[L''-H]^+[B(C_6F_5)_3Q]^-$
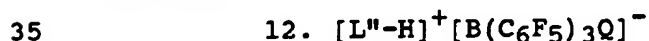
wherein:

F is fluorine, C is carbon and B, L', and Q are defined hereinabove. Illustrative but not limiting, examples of most preferred activator compounds comprising boron which may be used in the preparation of the improved catalysts of this invention include N,N-dialkylanilinium salts (L' = N,N-dialkylaniline) where Q is a simple hydrocarbyl such as methyl, butyl, cyclohexyl, or phenyl or where Q is a polymeric hydrocarbyl of indefinite chain length such as polystyrene, polyisoprene, or poly-paramethylstyrene. Polymeric Q substituents on the most preferred anion offer the advantage of providing a highly soluble ion-exchange activator component and final ionic catalyst. Soluble catalysts and/or precursors are often preferred over insoluble waxes, oils, phases, or solids because they can be diluted to a desired concentration and can be transferred easily using simple equipment in commercial processes.

Activator components based on anions which contain a plurality of boron atoms may be represented by the following general formulae:

13. $[L''-H]_c[(CX)_a(BX)_mX_b]^{c-}$ or

14. $[L''-H]_{d'}[[[(CX_6)_{a'}(BX_7)_{m'}(X_8)_{b'}]^{c'-}]_2M^{n'+}]^{d'-}$
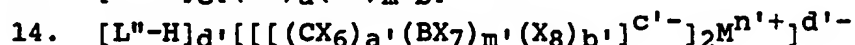
wherein

[L''-H] is either H+ or a Bronsted acid derived from the protonation of a neutral Lewis base;

X, X', X", X_6, X_7 and X_8 are, independently, hydride radicals, halide radicals, hydrocarbyl radicals, substituted-hydrocarbyl radicals, halocarbyl radicals, substituted-halocarbyl radicals, or hydrocarbyl- or halocarbyl-substituted organometalloid radicals;

M is a transition metal;

a and b are integers $\geq$ 0; c is an integer $\geq$ 1; aá+ábá+ cá= an even-numbered integer from 2 to about 8; and m is an integer ranging from 5 to about 22;

a and b are the same or a different integer 0; c
is an integer ≥ 2; a + b + c = an even-numbered integer
from 4 to about 8; m is an integer from 6 to about 12;
n is an integer such that 2cá- ná= d; and d is an
5   integer ≥ 1.

Preferred anions of this invention comprising a
plurality of boron atoms comprise:

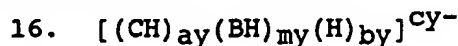(1) A trisubstituted ammonium salt of a borane or
carborane anion satisfying the general formula:
10   15. $[(CH)_{ax}(BH)_{bx}]^{cx-}$
wherein:

ax is either 0 or 1; cx is either 1 or 2; ax + cx
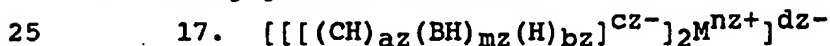= 2; and bx is an integer ranging from about 10 to 12;

(2) A trisubstituted ammonium salt of a borane or
15   carborane or a neutral borane or carborane compound
satisfying the general formula:
             16. $[(CH)_{ay}(BH)_{my}(H)_{by}]^{cy-}$
wherein:

ay is an integer from 0 to 2; by is an integer
20   from 0 to 3; cy is an integer from 0 to 3; ay + by + cy
= 4; and my is an integer from about 9 to about 18; or

(3) A trisubstituted ammonium salt of a
metallaborane or metallacarborane anion satisfying the
following general formula:
25   17. $[[[(CH)_{az}(BH)_{mz}(H)_{bz}]^{cz-}]_2 M^{nz+}]^{dz-}$
wherein:

az is an integer from 0 to 2; bz is an integer
from 0 to 2; cz is either 2 or 3; mz is an integer from
about 9 to 11; az + bz + cz = 4; and nz and dz are,
30   respectively, 2 and 2 or 3 and 1.

Illustrative, but not limiting, examples of second
components which can be used in preparing catalyst
systems utilized in the process of this invention
wherein the anion of the second component contains a
35   plurality of boron atoms (as in formulae 10-17) are
mono-, di-, trialkylammonium and phosphonium and
dialkylarylammonium and -phosphonium salts such as

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bis[tri(n-butyl)ammonium] dodecaborate, bis[tri(n-butyl)ammonium]decachlorodecaborate, tri(n-butyl)ammonium dodecachlorododecaborate, tri(n-butyl)ammonium 1-carbadecaborate, tri(n-butyl)ammonium
5   1-carbaundecaborate, tri(n-butyl)ammonium 1-carbadodecaborate, tri(n-butyl)ammonium 1-trimethylsilyl-1-carbadecaborate, tri(n-butyl)ammonium dibromo-1-carbadodecaborate; borane and carborane complexes and salts of borane and carborane anions such
10   as decaborane(14), 7,8-dicarbaundecaborane(13), 2,7-dicarbaundecaborane(13), undecahydrido-7,8-dimethyl-7,8-dicarbaundecaborane, tri(n-butyl)ammonium 6-carbadecaborate(12), tri(n-butyl)ammonium 7-carbaundecaborate, tri(n-butyl)ammonium 7,8-
15   dicarbaundecaborate and metallaborane anions such as tri(n-butyl)ammonium bis(nonahydrido-1,3-dicarbanonaborate)cobaltate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundecaborato) ferrate(III), tri(n-butyl)ammonium bis(undecahydrido-
20   7,8-dicarbaundecaborato) cobaltate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaunaborato) nikelate(III), tri(n-butyl)ammonium bis(nonahydrido-7,8-dimethyl-7,8-dicarbaundecaborato)ferrate(III), tri(n-butyl)ammonium bis(tribromooctahydrido-7,8-
25   dicarbaundecaborato)cobaltate(III), tri(n-butyl) ammonium bis(undecahydridodicarbadodecaborato) cobaltate(III) and bis[tri(n-butyl)ammonium] bis(undecahydrido-7-carbaundecaborato) cobaltate(III).
        A similar list of representative phosphonium compounds
30   can be recited as illustrative second compounds, but for the sake of brevity, it is simply noted that the phosphonium and substituted-phosphonium salts corresponding to the listed ammonium and substituted-ammonium salts could be used as second compounds in the
35   present invention.

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The preferred activator compounds comprising
Lewis-acid activators and in particular alumoxanes are
represented by the following general formulae:

18. $(R^3-Al-O)_p$

19. $R^4(R^5-Al-O)_p-AlR^6{}_2$

20. $(M')^{m+}Q'_m$
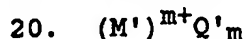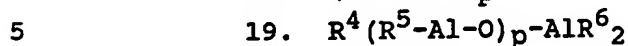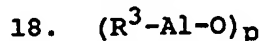
An alumoxane is generally a mixture of both the linear
and cyclic compounds. In the general alumoxane
formula, R^3, R^4, R^5 and R^6 are, independently a C_1-C_6
alkyl radical, for example, methyl, ethyl, propyl,
butyl or pentyl and "p" is an integer from 1 to about
50. Most preferably, R^3, R^4, R^5 and R^6 are, each
methyl and "p" is a least 4. When an alkyl aluminum
halide is employed in the preparation of the alumoxane,
one or more R^{3-6} groups may be halide. M' and M are as
described previously and Q' is a partially or fully
fluorinated hydrocarbyl.

As is now well known, alumoxanes can be prepared
by various procedures. For example, a trialkyl
aluminum may be reacted with water, in the form of a
moist inert organic solvent; or the trialkyl aluminum
may be contacted with a hydrated salt, such as hydrated
copper sulfate suspended in an inert organic solvent,
to yield an alumoxane. Generally, however prepared,
the reaction of a trialkyl aluminum with a limited
amount of water yields a mixture of both linear and
cyclic species of alumoxane.

Suitable alumoxanes which may be utilized in the
catalyst systems of this invention are those prepared
by the hydrolysis of a trialkylaluminum, such as
trimethylaluminum, triethylaluminum, tripropylaluminum,
triisobutylaluminum, dimethylaluminum chloride,
diisobutylaluminum chloride, diethylaluminum chloride
and the like. The most preferred alumoxane for use is
methylalumoxane (MAO). Methylalumoxanes having an
average degree of oligomerization of from 4 to 25 ("p"

29

= 4 to 25), with a range of 13 to 25 are the most
preferred.

It is recognized that an alumoxane is not a
discrete material. A typical alumoxane will contain

5 free trisubstituted or trialkyl aluminum, bound
trisubstituted or trialkyl aluminum, and alumoxane
molecules of varying degree of oligomerization. Those
methylalumoxanes most preferred contain lower levels of
trimethylaluminum. Lower levels of trimethylaluminum

10 can be achieved by reaction of the trimethylaluminum
with a Lewis base or by vacuum distillation of the
trimethyl aluminum or any other means known in the art.

It is also recognized that after reaction with the
transition metal compound, some alumoxane molecules

15 are in the anionic form as represented by equations 1-
3, and thus for our purposes, are considered "non-
coordinating" anions.

The activator compositions most preferred for
forming the ionic catalyst used in this process are

20 those containing a tetrapentafluorophenyl boron anion;
two or more tripentafluorophenyl boron anion groups
covalently bond to a central atomic molecular or
polymeric complex or particle; tripentafluorophenyl
boron; or methylalumoxane.

25   Other examples of activator specific compositions
which may be used to form an anionic catalyst useful in
this invention are identified and more fully described
in European Patent Application Nos. 0 277 003 and 0 277
004 and WO 92/00333 which are hereby incorporated by

30 reference.

CHOICE OF CATALYST

This invention relates to a process to produce
long chain branched polymers, to catalysts used to

35 produce long chain branched polymers and to the
polymers themselves. This invention relates to a
method for producing polymers with substantially linear

long chain branching comprising contacting, under
polymerization conditions, a vinyl terminated polymer
(macromonomer) with a chain length of 250 or more
carbons, with one or more olefin monomers and a
5 metallocene catalyst system comprising a mono, di, or
tri cyclopentadienyl transition metal catalyst
cocatalized with a non-coordinating anion or an
alumoxane or a Lewis acid activator. This invention
also contemplates a process for producing a branched
10 polymer comprising:

contacting in the presence of a polymerization
catalyst system,

(i) a macromonomer at least 250 carbons long
comprising one or more C_2-C_{30} olefinic monomer units
15 said macromonomer having chain end vinyl unsaturation,
and

(ii) a polymerizable olefinic monomer or
monomer mixture

under conditions to (co)polymerize the monomers
20 and incorporate the macromonomer into the growing
(co)polymer chain via the chain end unsaturation,

said catalyst system comprising mono-, di-, or
tri- cyclopentadienyl transition metal catalyst
cocatalized with a non-coordinating anion, an aluminium
25 alkyl, or an alumoxane.

The reaction is maintained at 70°C, more preferably 70
to 100°C, even more preferably at 90°C. The weight
ratio of macromonomer to olefin monomer present is
between about 1:1 to about 1:5, preferably about 1:1.5
30 to about 1:3, more preferably about 1:2.

The branched polymers of this invention are
comprised of a family of polyolefins and olefin
copolymers which are copolymerizable by metallocene
polymerization. Long chain branched polymers of this
35 type are made by copolymerization of vinyl terminated
polymers with the desired ethylenically unsaturated
monomer or monomers. The family of polyolefins

includes low to high density polyethylene or ethylene-
alpha-olefin copolymers as well as polypropylene and
polypropylene copolymers. The vinyl terminated
polymers useful in this invention include high density

5   polyethylene and polyethylene copolymers. Production
of these polymers gives control over the side-chain
molecular weight and composition. The branched
polymers of this invention can be a low-density
polyethylene with a high-density polyethylene branch.

10 They are also not limited to side-chains consisting of
the same polymer composition as the backbone. Likewise
it is comptemplated that the macromonomers can comprise
homopolymers or copolymers of olefins, particularly of
C_2 to C_{30} alpha olefins. specifically a copolymer or

15 polymer with more than 250 carbons that has vinyl
termination can be used. The metallocene catalysts
disclosed in this invention can produce vinyl-
terminated homopolymers and copolymers. However,
another method the produce vinyl termination is to

20 produce a polymer with an ethylene "cap" or end with
the needed vinyl group. This could be accomplished by
raising the reaction temperature at the "end " of the
reaction and simultaneously adding ethylene so that the
ethylene perefferientailly polymerizes to form an end

25 "cap" or block. A block copolymer of ethylene and a C_3
to C_{30} alpha olefin would also present the necessary
vinyl termination.

The main chain and the sidechains may be the same
of different olefin homo or copolymers. In particular

30 main and side chains of ethylene are preferred.
However main and side chains of ethylene copolymerized
with propylene, 1-butene, 1-pentene, 4-methylpentene-1,
1-hexene or 1-octene are also preferred.

The ability to prepare long-chain branched olefins

35 in which the side-chain compositions are significantly
different from the backbone adds a unique dimension to
the polymers of this invention

The branched polymers of this invention typically have a weight average molecular weight at or above 50,000, preferably 50,000 to 1,000,000 and a Mw/Mn of 6 or less. The vinyl terminated polymers (macromers)

5 that become the side chains in the branched polymers of this invention are typically more than 200 carbons long, preferably 250 to 3500, even more preferably 300 to 3000 carbons long. Further these side chains insert into the main chain at an average of up to 5 side

10 chains per 1000 main chain carbons, although it is statistically possible for a particular main chain to have no side chains. Also, as a benefit of utilizing titanium-containing monocyclopentadienyl transition metal catalysts in the catalyst system, a narrow

15 composition distribution of the side chains may be obtained. A narrow composition distribution means that among the individual polymer main chains the number of side chains are roughly similar. For example, three main chains with 2, 3, and 2 side chains respectively

20 have a very narrow composition distribution, while three main chains with 3, 9, and 20 sides chains, respectively, have a broad composition distribution. As an added benefit, if the main chain is a copolymer made using a titanium containing monocyclopentadienyl

25 metallocene catalyst, it will have a narrow composition distribution and higher comonomer incorporation than traditional coordination catalysts.

It is also contemplated by this invention that the vinyl terminated macromonomer can be produced in one

30 step of a continuous or series process which then proceeds to copolymerize the macromonomer with one or more alpha olefins. It is also comtemplated that the macromonomer can be produced separately by one process and then polymerized later in a separate similar or

35 different process.

CATALYSTS TO PRODUCE POLYMERS OF THE MACROMONOMER AND
AN OLEFIN

A large group of metallocene catalysts may be
selected from to produce both the vinyl terminated

5   polymers (macromers) and the branched polymers of this
invention. The choice of catalyst system is influenced
by the characteristics desired in the final product.
For example, a noncoordinating anion activation system
rather than MAO could be found to be preferable to

10   avoid isomerization problems, or the metallocene
catalyst Cp_2ZrMe_2 (bis cyclopentadienyl zirconium
dimethyl) with $(pfp)_3B$ (perflourotriphenyl boron) as
the cocatalyst activator could be chosen because of
this system's high activity at higher temperatures such

15   as 90°C and above. Further this catalyst system gives
high levels of vinyl ends during polymerization in
hexane and few or no vinyl ends when polymerized in
toluene. The resulting vinyl terminated polymers are
branched. This branching can be eliminated if a

20   sterically hindered catalyst like $(Me_5Cp)_2ZrMe_2$ (bis
pentamethylcyclopentadienyl zirconium dimethyl) is
used. This catalyst system sterically inhibits the
copolymerization of vinyl terminated polymers. It
should be noted that the vinyl terminated macromonomers

25   of this invention can be branched. However the level
of this branching does not approach a dendritic
structure. These macromers and those that have
little or no side chain branching or are substantially
linear will be referred to as linear.

30   The catalyst choices for copolymerization of vinyl
terminated polymers with other monomers are also large
and include catalyst systems containing bridged and
unbridged bis cyclopentadienyl transition metal
compounds as well as monocyclopentadienyl transition

35   metal compounds. Monocyclopentadienyl transition metal
catalysts are preferred as they polymerize large
"monomers" well. For example, monocyclopentadienyl

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(Mono Cp) transition metal catalysts, particularly
titanium, incorporate more monomer than coordination
catalysts. Thus one would choose a Mono Cp Ti catalyst
to make lower density products over the

5   Tris(perfluorophenyl)Boron activated systems utilized
in example 1 and 2 to make high density material.

To understand the advantages of polymers produced
in accordance with the present invention, some general
discussions of the properties of polymer solids and

10   melts is helpful. Molten polyethylene is highly
viscous. The viscosity is a function of weight-average
molecular weight (M_w); molecular weight distribution
(M_w/M_n), also called the index of polydispersity; and
the shear rate exerted on the polymer. The molecular

15   weight values are in part related to branching of the
polymer. Molten polyethylene is classified as a
pseudoplastic fluid, which means that its viscosity
decreases with increasing shear rate. The relationship
between viscosity and shear rate depends upon the

20   molecular weight distribution and degree of long chain
branching of the polymer. Polymers having a broad
molecular weight distribution tend to have lower
viscosity values at conditions of high shear rates than
polymers having a narrow molecular weight distribution

25   while having equivalent viscosities at conditions of
low shear rates.

As noted, viscosity as a function of shear rate is
also dependent upon the degree of long chain branching
of a polymer which affects molecular weight

30   distribution. In general, a polymer with long chain
branching will have higher viscosity values at low
shear rates and lower viscosity values at high shear
rates compared to an unbranched polymer with equivalent
molecular weight. Lower viscosity at high shear rates

35   means the long chain branched polymer can be extruded
at lower temperatures and at a higher rate which
results in less energy consumption.

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From a processability viewpoint, it is usually
desirable to have a polymer which displays high
viscosity at low shear rates and low viscosity at high
shear rates, in other words, it is desirable to have a
5   polymer that processes with the characteristics of a
branched polymer at conditions of low shear while
having the processing characteristics of a. broad
molecular weight distribution branched polymer at
conditions of high shear. This combination of
10   properties is often sought by broadening the molecular
weight distribution of a polymer by introducing long
chain branching.

The inventors have found that the positive
viscosity processing characteristics of a polymer at
15   both ends of the shear rate range may be achieved by
polymers in accordance with the present invention. The
predictable solid polymer mechanical properties
achievable by polymers in accordance with the present
invention are good impact and tear resistance, good
20   environmental stress crack resistance (ESCR) values,
good tensile properties, good modulus/density balance,
good reblock/density balance, and good clarity,
relative to linear polyethylenes without long chain
branching.

25   This unique balance of favorable polymer melt
processability and solid polymer mechanical
characteristics is achieved through the creation of
remote long chain branching at a frequency and length
great enough to impart processability characteristics
30   of LDPEs but at a low enough frequency so as not to
destroy the superior solid polymer physical
characteristics of LPEs. In particular, this balance
is achieved by the introduction of some linear long
chain branches having a average molecular weight
35   greater than the critical molecular weight for
entanglement (M_c) of the polymer with a linear long
chain branching frequency less than 5.0 branches per

1,000 carbon atoms of the main polymer chains. These
polymers may be produced over a wide range of molecular
weight distributions (M_w/M_n) (index of polydispersity)
of 2.0 to 10. Preferably, the frequency of long chain

5   branching is less than 5 branches per 1,000 carbon
atoms of the main polymer chains (preferably an average
frequency of 0.2 to 3 chains per 1000 C, atom, even
more preferably an average frequency of 0.9 to 2 chains
per 1000 C, even more preferably an average frequency

10   of 1 to 2 chains per 1000 C) with a preferred molecular
weight distribution range of about 2 to about 6, more
preferably 2 to 4.

    These advantageous properties can be achieved when
even 5 or more weight percent of the composition is

15   "branched." This may occur when a branched polymer is
blended with another polymer or when the branched
polymer is part of a reactor blend. Preferably the
branched polymer is present at least 5 weight percent,
even more preferably at least 10 weight percent, even

20   more preferably at least 40 to 70 weight percent.

    The viscosity characteristics of polymers of the
present invention are not the only processing
advantages. Another advantage of polymers having
linear long chain branching in accordance with the

25   present invention are the superior elastic
characteristics of the polymer melt. Molten
polyethylene exhibits elastic properties over a wide
temperature range. After molten polyethylene passes
through the die of an extruder under pressure, the

30   strand of polyethylene increases in diameter or
thickness. This is known as extrudate swell. At low
shear rates, extrudate swell increases as molecular
weight and long chain branching increase. In other
words, extrudates typically swell as molecular weight

35   distribution broadens.

    Polymers produced in accordance with the present
invention exhibit increased extrudate swell. The

significance of this increased extrudate swell is that
is a reflection of what is known as the elastic nature
of the polymer. The elastic nature of the polymer is
very important in certain polymer melt extrusion
5   processes such as the manufacture of tubular film,
chill roll casting and extrusion coating in which an
extruded web of film is produced which is stretched in
the direction of flow. Such extrusion processes can
only be carried out with materials that are able to
10   sustain a tensile stress on the melt. In other words,
it is important that the polymer melt be somewhat
elastic. There should be a balance between the
elasticity of the polymer melt and the viscosity in
blow molding operation. The balance between elasticity
15   and viscosity of the polymer melt affects polymer
parison integrity. If the balance of properties is in
favor of viscosity over elasticity, the polymer melt
will not have good stability and tend to sag during
certain extrusion processes. There is a strong
20   correlation between extrudate swell ratios and parison
integrity. The introduction of long chain branching in
accordance with the present invention results in
polymer melts having swell ratios indicative of good
elastic properties for extrusion processes.
25   The presence of a small amount of long chain
branching in a linear molecule increases elasticity of
the polymer melt by introducing very long relaxation
times in the relaxation spectrum of the melt. Since
the polymer melt is a collection of molecules with
30   different lengths and different branches, each molecule
will respond differently to a given deformation. The
collection of response times is referred to as the
relaxation time spectrum which directly relates to the
stability of the polymer melt during extrusion.
35.   Long chain branching in accordance with the
present invention has another important advantage of
changing the elongational characteristics of polymer

melts. The presence of long chain branching increases
the value of the longational viscosity and introduces a
maximum elongation viscosity as a function of strain
rate.

5   The polymers produced in accordance with the
present invention have still another advantage of
having a reduced tendency to melt fracture at high
shear rates. Smooth extrudates of polymer melts may be
obtained easily at low shear rates. However, above a
10   critical shear rate, the extrudate becomes uneven. The
form of distortion of the extrudate varies. In some
cases, the extrudate has the form of a screw thread, in
others, the extrudate becomes spiral twisted while in
others the distortion may take on the affect of a
15   regular ripple or even random distortions. The
critical shear rate of a polymer is related to the
degree of entanglement of the polymer. The greater the
degree of entanglement of the polymer, the lower the
critical shear rate. Since the polymers produced in
20   accordance with the present invention, due to the
linear long chain branching, have less entanglement
than linear polymers, the critical shear rate of these
polymers will be increased. The result is that
polymers made in accordance with the present invention
25   have a reduced tendency to melt fracture at high shear
rates than conventional linear polymers.

       The polymers of the present invention also enjoy
the good solid polymer mechanical properties associated
with short chain branching distributions of single
30   site catalyst polymerizations. The polymers produced
in accordance with the present invention may have high
molecular weights with narrow molecular weight
distributions. These narrow distributions result in
products having lower extractables caused by amorphous
35   waxes, better clarity due to the absence of large light
refracting crystals, and superior impact resistant due

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to increased number of tie molecules binding crystal
regions together.

The frequency of chain branching is determined by
13C NMR spectrometry for homopolymers and by measuring
5   the viscous energy of activation of copolymers with a
parallel plate oscillating shear melt rheometer.

Long chain branching may be detected by comparing
the results of different gel permeation chromatography
(GPC), measured with both a refractive index detector
10   and a low angle laser light scattering detector. GPC
separations are governed by the hydrodynamic volume of
polymeric molecules in solution. The standard detector
on most GPCs measures the relative refractive index
(RI) of the effluent. The RI detector assumes that
15   molecules coming off the separation column at Time 1
have the same molecular weight as molecules eluting
from an unbranched calibration standard at Time 1. It
has been discovered that long chain branches do not
increase the hydrodynamic volume of a molecule by an
20   amount proportional to the length of its branches. It
is believed that the contribution in the hydrodynamic
volume is only a fraction of the branch length. In
other words, refractive index detectors cannot "see"
linear long chain branches in accordance with the
25   present invention. However, a low angle light
scattering (LALLS) detector does "see" all carbons in a
polymer molecule. By analyzing a sample with both
detectors, the difference in the results provides
evidence of long chain branching in accordance with the
30   present invention. This technique is illustrated by
the following data:

Sample	Mw (DRI detector)	Mw (LALLS detector)
A	99800	99900
B	111000	116000
C	206000	231000

.35

●   ●

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Sample A is an ethylene-hexene copolymer made in a
gas phase process with a metallocene catalyst which is
known to have no long chain branches. By comparing the
molecular weight values calculated by the standard
5   refractive index detector (RI) and the LALLS detection
method, one sees that there is no significant
difference in the values suggesting there are no hidden
branches. Comparing the RI and LALLS values for sample
B, an increase of 5,000 in molecular weight is seen by
10   the LALLS detection method. With sample C, a 25,000
molecular weight increase is detected. The higher
molecular weight of samples B and C as determined with
the LALLS detector are evidence of long chain
branching.
15   By comparing the different GPC techniques for
polymers in accordance with the present invention, one
generally sees that molecular weight as calculated by
the LALLS technique is greater than the molecular
weight as calculated by the RI GPC technique.
20   Long-chain branching in polyethylene is defined as
those branches which produce one or more of the
following effects.

1. High viscous energy of activation (Ea).

25   Polymer viscous energy of activation can be
determined with parallel plate shear melt rheometry.
Melt viscosity-temperature dependence is determined by
performing shear rate superposition. The resulting
shift factors are fitted to an Arrhenius equation; the
30   product is the viscous energy of activation.
The energies of activation for a variety of
polyethylene types are illustrated in the bar chart of
figure 1. HDPE represents narrow MWD, linear
homopolymers in the 5-50 MI range. LLDPE represents
35   narrow MWD, linear ethylene-butene copolymers with
comonomer content ˜12% and MI in the 1-2 dg/min range.
HMW-HDPE represents narrow MWD, linear ethylene

homopolymers with Mw's greater than 200k (i.e., MI <
0.2 dg/min). LDPE represents long-chain branched,
ethylene homopolymers produced in a free-radical
process. The LPE w/ LCB represents some of the branched
5   polymers of this invention.

The unusually high Ea of the LPE w/ LCB is clear
evidence of long-chain branching.

2. Low viscosity, moderate shear rates relative to
10 unbranched NMWD linear polymers.

Melt viscosities can be measured vs. shear rate
with a capillary rheometer. Figure 2 is an illustration
of the relationship between the Mw of NMWD linear
polyethylenes, and their melt viscosity measured at
15   340 s^{-1} and 190°C. This data is narrowly distributed
about a linear model: viscosity = 0.0115 x Mw - 325.
The position of the LDPE samples reflects the known
fact that LDPEs are more "shear thinning" than linear
polyethylenes, i.e., their viscosities decrease more
20   rapidly as shear rate increases than do the viscosities
of linear polyethylenes. The position of the LPE w/ LCB
is clear evidence that this NMWD linear homopolymer
contains long-chain branching. The branched polymers of
this invention have a viscosity measured at 340sec-
25   1/190°C of 0.75(0.0115 x Mw - 325).

3. High melt strength.

Melt strength can be determined with a Rheotens
Instrument which consists of a capillary rheometer
30   equipped with an accelerating wheel take-off station.
The melt tensile force in the capillary rheometer
extrudate is measured as a function of the
instantaneous wheel velocity. Figure 3 illustrates the
relationship between melt tension, measured at 190°C
35   immediately before the onset of severe draw resonance,
and Mw for numerous unbranched, narrow MWD linear
ethylene-alpha-olefin copolymers. These tensile forces

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are narrowly distributed about a linear model: melt
tensile force = (7.68×10^{-5}) x Mw - 4.32. The
branched polymers of this invention will exhibit a melt
tensile force of $1.3((7.68 \times 10^{-5})$ x (Mw of the
5   polymer) - 4.32).

        The unusually high tensile force observed with the
LDPE is attributed to its long-chain branching.
Evidence of the maximum frequency of the long-chain
branches in a linear polymer can be determined with
10   carbon-13 NMR if the polymer contains no short-chain
branches, due to the comonomer, which are larger than 3
carbons in length. The carbon atom in the polymer's
backbone to which a branch, which is larger than 3
carbons in length, is attached produces a signal in the
15   C13-NMR spectrum at 38 ppm, which is distinguishable
from all other carbons in the qualifying test sample
and therefore a measure of the maximum number of long-
chain branch points.

        The present invention may be illustrated by the
20   following examples:

EXAMPLE 1 Macromer A
        A one liter autoclave solution polymerization
reactor was charged with 400 ml toluene, 40 psig
25   ethylene, and 58.9mg Cp_2ZrMe_2 & 11mg B(pfp)3
[Bis(cyclopentadienyl)Zirconiumdimethyl & tris
(pentaflurophenyl) Boron)]. The mixture was reacted at
90°C (16° exotherm) for 0.87 hours. The polymerization
yielded 121.4 grams of polymer after drying in a vacuum
30   oven for 24 hours until odor-free. The dried polymer
consisted of irregularly-shaped particles ranging in
size from less than 0.1 mm to greater than 1 cm. The
density of the polymer was 0.953 g/cm^3, with a weight-
average molecular weight (M_w) of 29,000 with a level of
35   vinyl that was not detected by NMR, and an index of
polydispersity (M_w/M_n) of 3.28. The polymer had a
chain branching frequency of 0.48 branches per 1,000

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carbon atoms of the main polymer chains by ^{13}C NMR analysis.

EXAMPLE 2 Polymerization with Macromer A

5   A one liter solution polymerization autoclave reactor was charged with 400ml toluene, 25g of macromer A produced in example 1 (linear ethylene homopolymer having a weight-average molecular weight (M_w) of 29,000 with very low levels, i.e. not detected, of vinyl

10   unsaturations per 1,000 carbon atoms) and 100 psig ethylene, and 0.24 millimoles of bis (cyclopentadiene) dimethyl zirconium tris (pentafluorophenyl) boron catalyst (in toluene) with an initial reactor temperature of 45°C. The solution temperature was

15   raised to 102°C and reacted for 0.33 hours. The polymerization yielded 57.0 g of polymer after drying in a vacuum oven for 24 hours until odor-free. The dried polymer consisted of irregularly-shaped particles ranging in size from less than 0.1 mm to greater than

20   1.0 cm. The density of the polymer was 0.953 g/cm^3, with a weight-average molecular weight (M_w) of 82,500 and an index of polydispersity (M_w/M_n) of 5.3 The polymer had a long chain branching frequency of 2 long chain branches per 1,000 main chain carbon atoms by ^{13}C

25   NMR analysis.

EXAMPLE 3 Macromer B

      A one liter autoclave solution polymerization reactor was charged with 400 ml of hexane, 20 psig

30   ethylene, and 60 mg of bis (cyclopentadiene) dimethyl zirconium catalyst and 60 mg of tris (pentafluoronyl) boron catalyst activator. The mixture was reacted at 90°C for 0.7 hours. The polymerization yielded 26g of polymer after drying in a vacuum oven for 24 hours

35   until odor-free. The weight-average molecular weight (M_w) of the polymer was 21,000 and the index of polydispersity (M_w/M_n) was 8.2. The polymer had a

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chain branching frequency of 1.22 branches per 1,000
main chain carbon atoms of the main polymer chains by
^{13}C NMR analysis.

5   **EXAMPLE 4 Polymerization with Macromer B**
        A one liter autoclave solution polymerization
reactor was charged with 400ml. of toluene,. 25g macromer
B produced in example 3(linear ethylene homopolymer
having a weight-average molecular weight (M_w) of 21,000
10   and 1.0 vinyl unsaturations per 1,000 carbon atoms) and
50 psig ethylene, and 0.24 milimoles bis
(cyclopentadiene) dimethyl zirconium tris
(pentafluorophenyl) boron catalyst (in toluene). The
mixture was reacted at 60°C (42° exotherm)for 0.28
15   hours. The polymerization yielded 78.8g of polymer
after drying in a vacuum oven for 24 hours until odor-
free. The weight-average molecular weight (M_w) was
32,000 and index of polydispersity or MWD, (M_w/M_n) was
3.0. The polymer had a linear long chain branching
20   frequency of 0.48 branches per 1,000 carbon atoms of
the main polymer chains by ^{13}C NMR analysis.

CLAIMS

What is claimed is:

1.   A branched polyolefin comprising:

         a main chain (b) of a homopolymer or a
5   copolymer of C2 - C30 alpha olefins; and

         side chains (a) of at least 250 carbon atoms
         comprising a homopolymer or a copolymer of C_2 -
         C_{30} alpha olefins, said side chains being
         distributed along the polymer main chain at an
10   average frequency of 0.1 to 5 side chains per 1000
         main chain carbon atoms,

         said branched polymer having a weight average
         molecular weight of at least 30,000 and an M_w/M_n
         of 6 or less.

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2. The branched polyolefin of claim 1 wherein the side
   chains(a) are 300 to 3000 carbons long.

3.   The branched polyolefin of claim 1 or 2 having a Mw
20   of 30,000 to 1,000,000.

4.   The branched polyolefin of any previous claim
      having a Mw/Mn between 1 and 4.

25   5.   The branched polyolefin of any previous claim
            having side chains(a) present at an average frequency
            of 0.2 to 3 side chains per 1000 main chain carbons.

6. The polyolefin of any previous claim wherein the
30   side chains (a) derive from ethylene and any C_3 to C_{30}
     alpha olefin and the main chain, independently, derives
     from ethylene and any C_3 to C_{30} alpha olefin.

7. The branched polymer of any previous claim
35   characterized by a density of 0.85 to 0.95g/cm^3.

8. The branched polymer of any previous claim wherein the side chains (a) comprise block copolymer of ethylene and propylene.

5   9. The polymer of any previous claim wherein the side chains (a) comprise a polymer of any C_3 to C_{30} alpha olefin with an ethylene block present at the insertion point along the main chain.

10   10. A polymer blend composition comprising at least 5 weight percent, based upon the weight of the composition, of a branched polyolefin of any previous claim.

15   11. A film or article of manufacture comprising the branched polymer of any previous claim.

12. A method for producing polyolefins of claims 1-10 comprising the steps of:

20   1)   contacting under polymerization conditions :
            one or more alpha olefin monomers with a catalyst system to produce a vinyl terminated macromonomer of at least 250 carbon atoms long;

25   2)   subsequently contacting, under polymerization conditions:
            said vinyl terminated macromonomer; with one or more alpha olefin monomers; and a catalyst system comprising a cyclopentadienyl

30   transition metal catalyst and a cocatalyst or activator.

13. The method of claim 12, wherein the transition metal is Zr, Hf, or Ti.

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14. The method of claims 12 or 13, wherein the cocatalyst activator is an alumoxane or a Lewis acid activator.

5   15. The method of claims 12, 13, or 14 wherein the polymerization conditions for step 2) are solution, gas phase, bulk phase, or supercritical phase polymerization conditions.

10 16. A branched polyolefin of claim 1 having energy of activation greater than about 9 kcal/mole or a viscosity of 0.75X(0.0115 x Mw of the polymer -325) and a melt strength 1.3x((7.68 x 10^{-5}) x Mw-4.32).

15 17. The method of claims 12 - 15, wherein the cyclopentadienyl transition metal catalyst is a transition metal compound comprising a single cyclopentadienyl group and a heteroatom containing group each bonded to the transition metal, said
20 cyclopentadienyl group and heteroatom containing groups optionally bridged through a divalent moiety.